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# DETERMINATION OF 25 ELEMENTS IN BIOLOGICAL STANDARD REFERENCE MATERIALS BY NEUTRON ACTIVATION ANALYSIS

by

G. GUZZI, R. PIETRA and E. SABBIONI

1974


Joint Nuclear Research Centre
Ispra Establishment - Italy
Chemistry Division

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The study has been performed by the use of neutron activation analysis. Due to the very low concentration of some elements, radiochemical group or elemental separation procedures were necessary.

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The paper describes the techniques used to analyse 25 elements. Computer assisted instrumental neutron activation analysis with high resolution Ge(Li) spectrometry was considerably advantageous in the determination of Na, K, Cl, Mn, Fe, Rb and Co and in some cases of Ca, Zn, Cs, Sc and Cr.

For low contents of Ca, Mg, Ni and Si special chemical separation schemes, followed by Cerenkov counting have been developed. Two other separation procedures allowing the determination of As, Cd, Ga, Hg, Mo, Cu, Sr, Se, Ba and P have been set up. The first, the « simplified » one involves the use of high resolution Ge(Li) detectors, the second, the more « complete » one involves a larger number of shorter measurements performed by simpler and more sensitive techniques, such as NaI(Tl) scintillation spectrometry and Cerenkov counting.

The results obtained are presented and discussed.

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## ABSTRACT

« Standard and Certified Reference Materials » programme of the JRC includes the determination of trace elements in complex biological samples delivered by the U.S. National Bureau of Standards : Bovine Liver (NBS SRM 1577), Orchard Leaves (NBS SRM 1571) and Tomato Leaves.

The study has been performed by the use of neutron activation analysis. Due to the very low concentration of some elements, radiochemical group or elemental separation procedures were necessary.

The paper describes the techniques used to analyse 25 elements. Computer assisted instrumental neutron activation analysis with high resolution Ge(Li) spectrometry was considerably advantageous in the determination of Na, K, Cl, Mn, Fe, Rb and Co and in some cases of Ca, Zn, Cs, Sc and Cr.

For low contents of Ca, Mg, Ni and Si special chemical separation schemes, followed by Cerenkov counting have been developed. Two other separation procedures allowing the determination of As, Cd, Ga, Hg, Mo, Cu, Sr, Se, Ba and P have been set up. The first, the « simplified » one involves the use of high resolution Ge(Li) detectors, the second, the more « complete » one involves a larger number of shorter measurements performed by simpler and more sensitive techniques, such as NaI(Tl) scintillation spectrometry and Cerenkov counting.

The results obtained are presented and discussed.

CONTENTS

## 1. INTRODUCTION

The "Standard and Certified Reference Materials" programme of the Joint Research Centre includes, amongst other studies, the determination of trace elements in complex biological samples such as Bovine Liver (NBS SRM 1577), Orchard Leaves (NBS SRM 1571) and Tomato Leaves (NBS material)[1].

For its high sensitivity to a great number of elements of biological and toxicological concern, neutron activation analysis has been used to perform this study.
Computer aided instrumental neutron activation analysis together with high resolution Ge(Li) spectrometry has been considerably advantageous in the determination of Na, K, Cl, Mn, Fe, Rb, Co, and in some cases of Ca, Zn, Cs, Sc, and Cr as well. Other elements such as As, Cd, Ga, Hg, Mo, Cu, Sr and Se are present in such low concentrations that radiochemical group separation procedures were necessary before counting their activities.

For low contents of Ca, Mg, Ni and Si special chemical separation schemes, followed by Čerenkov counting, have been developed.
Two different separation schemes have been set up. The first, the "simplified" one involves the use of high resolution Ge(Li) detectors; the second, the more "complete" one involves a larger number of shorter measurements, performed by simpler and more sensitive techniques such as NaI(Tl) scintillation spectrometry and Čerenkov counting.

## 2. PROCEDURES

### 2.1 Materials and Equipment

U.S. National Bureau of Standards SRM 1577 (Bovine Liver), SRM 1571 (Orchard Leaves) and Tomato Leaves, also prepared by the NBS, were used for analysis.

For the elements where satisfactory consistent values were obtained in Bowen's Kale intercomparison exercise[7, 8], this material was used as a standard. For all other elements, weighed amounts of element to be determined were used as synthetic standard.

Irradiations were performed in the ISPRA-1 reactor.
For short-lived nuclides ($t_{1/2} \leq 15$ h) 200 mg samples were irradiated for 5 min in a pneumatic facility at a thermal neutron flux of $5 \times 10^{12}$ n/cm$^2$ s. For Ca, Mg, Ni and Si determination, 200 mg samples were irradiated in the same facility for 2 h.
For long-lived nuclides 200 mg samples were irradiated for 48 h in another pneumatic facility at a thermal neutron flux of $10^{13}$ n/cm$^2$ s.

Samples and standards were sealed in high purity quartz ampoules for long irradiations or in small polyethylene vials for shorter irradiations. Before opening, the quartz ampoules were cooled in liquid nitrogen to depress eventual internal pressures.

Materials used in chemical separation are:

- Acid aluminium oxide (AAO), chromatographic grade by Woelm, Eschwege, Germany;
- Hydrated antimony pentoxide (HAP) by Carlo Erba, Milan, Italy;
- Cuprous sulphide (CUS) by Carlo Erba, Milan, Italy;
- Tin dioxide (TDO) by Carlo Erba, Milan, Italy;
- Dowex 1x8 (100-200 mesh) by Baker Chemical Company, USA;
- Dowex 50x8 (100-200 mesh) by Baker Chemical Company, USA.

All other reagents of Analar Grade are used.

The apparatus used for the dissolution and distillation of biological materials was a modified version of the one proposed by Bethge[9] and used by Sjöstrand[10] and Sivasankara Pillay et al.[11]. It is shown in Fig. 1.

## 2.2 Counting and Data Processing

The irradiated samples and standards were measured either by means of gamma ray spectrometry, or by the Čerenkov counting technique.

### 2.2.1 Gamma Ray Spectrometry

The counting equipment used for this study was a 18 $cm^3$ coaxial Ge(Li) detector alternatively connected either with a small Laben 70 computer or with a Laben 4096 channel analyser.

Laben 70 has a 8 K memory capacity (16 bit) and performs the acquisition of gamma ray spectra, their elaboration and the printing out of the results. Peripherals include a 4096 channels analog-to-digital converter, an amplifier, an oscillographic display, a real time clock and an Olivetti TE 300 teleprinter.

Data reduction is accomplished by analysing successive sections of 128 channels. Each section is composed of the last 64 channels of the preceeding section, plus 64 new channels, thus avoiding the loss of peaks falling between two sections[2].

Only half of the memory (2048 channels) of the Laben multichannel analyser is currently used. To avoid gain shifts during long counting periods, a spectrum stabiliser has been connected to the analyser. Both counting equipments are provided with a 1 keV/channel gain setting.

Gamma ray spectra obtained with the multichannel analyser are stored

on punched paper tapes and then processed in batch mode by means of an IBM 370/165 computer.
An alternative to this mode of operation is the possibility of using an interactive on-line processing through an IBM 1070 System connected to the central computer, which allows the immediate reduction of the gamma spectra and the printing out of the results on an IBM 2741 teletypewriter.

The computer program called GRETEL[3], developed through the years as experience has progressed, performs the automatic finding of gamma peaks present in the spectra and gives all peak parameters (limits, centroid, net area, FWHM, error, energy attribution).

With batch processing either qualitative or quantitative analysis is possible. This last one is carried out using special "oriented" libraries which are prepared for each particular problem by the analyst himself. Besides, a drawing of the spectrum is obtained showing whether it has been correctly processed[4], or not.

When chemical separation procedures are performed, low resolution spectrometry (NaI(Tl) detectors) has been preferred due to its highest sensitivity. Quartz & Silice 3 x 3 " integral lines connected with Laben 512 channel analysers were used. Also in this case, the gamma spectra can either be punched on paper tapes and processed in batch mode, or processed on-line with the central computer.

Each counting system is equipped with automatic sample changers, controlled by the multichannel analysers or by the Laben 70 mini-computer, which allow repetitive cycles of measurements without any operator intervention.

### 2.2.2 Čerenkov Counting Technique

A liquid scintillation spectrometer (Intertechnique SL 30) was used[5].

The percent Čerenkov counting efficiency versus $\beta^-$ energy and the NaI(Tl) efficiency versus gamma energy, are given in Fig. 2. As an example, the values for Ca→Sc, Mg, Na, P, Si and Zn are also reported.
Table I gives the equilibrium counting rates of both techniques for the elements measured by the Čerenkov method in this study.

The ratios show the evident advantage of using this technique compared to the gamma ray spectrometry with NaI(Tl) detectors, although more sophisticated chemical separations are required.

TABLE I - Comparison Between Čerenkov and NaI(Tl) Detector Equilibrium Counting Rates

| Element | Measured Nuclide | Percentage Čerenkov Efficiency | Equilibrium Counting Rates | | | | $R = \frac{\text{Čerenkov}}{\text{NaI(Tl)}}$ |
|---|---|---|---|---|---|---|---|
| | | | Čerenkov | Beta energy keV (*) | NaI(Tl) | Gamma energy keV | |
| As | $^{76}As$ | 80.5 | $1.61 \cdot 10^{7}$ | | $8.8 \cdot 10^{5}$ | 559.2 | 18.25 |
| Ca | $^{49}Ca \rightarrow ^{49}Sc$ | 59.0 | $1.06 \cdot 10^{4}$ | 2010.0 | pure Beta | | - |
| Cd | $^{115}Cd$ | 14.0 | $1.4 \cdot 10^{5}$ | | $4.02 \cdot 10^{4}$ | 492.5<br>527.7 | 2.54 |
| Ga | $^{72}Ga$ | 35.2 | $4.52 \cdot 10^{6}$ | | $5.9 \cdot 10^{5}$ | 834.1 | 5.96 |
| K | $^{42}K$ | 75.3 | $6.32 \cdot 10^{5}$ | | $5.3 \cdot 10^{3}$ | 1524.7 | 112.0 |
| Mg | $^{27}Mg$ | 53.3 | $4.48 \cdot 10^{4}$ | 1620.0 | $3.53 \cdot 10^{3}$ | 844.0 | 12.7 |
| Mo | $^{101}Mo \rightarrow ^{101}Tc$ | 53.45 | $3.95 \cdot 10^{4}$ | | $9.59 \cdot 10^{2}$ | 300.0 | 41.3 |
| Na | $^{24}Na$ | 47.5 | $4.04 \cdot 10^{6}$ | 1394.0 | $3.4 \cdot 10^{5}$ | 1368.4 | 11.9 |
| Ni | $^{65}Ni$ | 20.5 | $2.15 \cdot 10^{4}$ | | $6.14 \cdot 10^{2}$ | 366.5 | 35.2 |
| P | $^{32}P$ | 50.0 | $1.23 \cdot 10^{6}$ | 1710.0 | pure Beta | | - |
| Si | $^{31}Si$ | 40.5 | $1.74 \cdot 10^{4}$ | 1480.0 | 1.26 | 1266.0 | 13800.0 |
| Zn | $^{69m}Zn \rightarrow ^{69}Zn$ | 12.6 | $1.26 \cdot 10^{4}$ | 914.0 | $1.19 \cdot 10^{4}$ | 438.7 | 1.06 |

(*) Beta energies are reported for the elements decaying with emission of only one $\beta^-$ particle, and for pure $\beta^-$ emitters. No $\beta^-$ energies are indicated in case of emission of several $\beta^-$.

## 2.3 Instrumental Nuclear Activation Analysis (INAA)

The irradiated samples and standards were transferred to polyethylene vials and counted with a Ge(Li) detector for 30 min (short irradiations) after a 1 h decay, and for 5 h (long irradiations) after a 10 days decay.
Short irradiated samples, after a decay of at least 2 weeks, were counted again to measure the Čerenkov radiation of $^{32}P$ induced in the walls of the polyethylene vials.

Two weeks decay are largely sufficient to allow the short-lived interfering radionuclides ($^{24}Na$, $^{38}Cl$, $^{42}K$) to reach decay to negligible levels.

Na, K, Cl and Mn were determined by INAA with short irradiations. Fe, Rb, Co and Zn were determined by INAA with long irradiations in Bovine Liver; Fe, Rb, Co, Cr, Cs, Ba, Ca, Sb and Sc in Orchard Leaves and finally Fe, Rb, Co, Cr, Cs, Ca, Sb, Ba and Sc in Tomato Leaves. Non destructive analysis of phosphorus by INAA has recently been applied by Sabbioni et al.[6] for biochemical applications. The presence of interfering radionuclides with different spectral shapes can be detected by a change of the ratio of the channels counting rates. We have additionally checked the radiochemical purity of the irradiated sample by repeating the measurement after a few days and checking for the expected $^{32}P$ decay.

## 2.4 Destructive Activation Analysis

### 2.4.1 Determination of Ca, Mg, Ni and Si

a) Determination of Mg and Ni:

1. Dissolve the irradiated sample (200 mg) with 5 ml of fuming $HNO_3$ adding at the boiling point drops of $H_2O_2$ up to 3 ml. Evaporate and repeat the operation with fuming $HNO_3$ and $H_2O_2$ until the solution becomes perfectly clear.

2. Evaporate again and dissolve with 10 ml of 0.1 M $HNO_3$ containing 50 µg carrier of $Ni^{++}$. Pass through an HAP column (10 mm dia. and 40 mm long) and a Dowex 50x8 column (8 mm dia. and 2.5 mm long). Wash both columns with 40 ml of 0.1 M $HNO_3$.

3. Mg and Ni are eluted from Dowex column with 20 ml of 3 M $HNO_3$.

4. The eluate is measured with the Čerenkov counting technique to determine immediately $^{27}Mg$, and after two or more hours $^{65}Ni$.

b) Determination of Ca (measurement of $^{49}Sc$ from $^{49}Ca$ decay):

1. Dissolve as for Mg and Ni with 5 µg carrier of $Sc^{+++}$.

2. Evaporate and dissolve with 10 ml of 6 M $HClO_4$. Wait 2 h for the decay of $^{49}Ca$ into $^{49}Sc$, then absorbe on a Dowex 50x8 column (8 mm dia. and 40 mm long) and wash with 20 ml of 10 M HCl.

3. $^{49}Sc$ is eluted with 20 ml of 6 M HF.

4. Count the eluate with Čerenkov technique.

c) Determination of Si:

1. Dissolve the sample as for the preceding separations.

2. Bring to almost dryness and add 10 mg of sodium silicate plus 10 ml of concentrated $HClO_4$. Filter the $SiO_2$ and wash with 50 ml of concentrated $HClO_4$.

3. Dissolve again the $SiO_2$ with 20 ml of 6 M HF and count with the Čerenkov technique.

2.4.2 Radiochemical Separation Schemes

a) Dissolution and Distillation Procedure:

The dissolution - distillation procedure for biological matrices in radiochemical separation schemes, used in this laboratory can be summarised as follows:

1. Add 2 ml of concentrated $H_2SO_4$, 5 ml fuming $HNO_3$ and 10 mg carrier of Au to 100-300 mg of irradiated sample, contained in the dissolution flask (see Fig. 1 ).
2. Boil for 10 min and collect the distillate in the upper reservoir of the flask.
3. Cool and recycle the distillate.
4. Boil for 10 min under reflux.
5. Boil for 10 min collecting the distillate.
6. Cool and add 5 ml fuming $HNO_3$.
7. Repeat operations 2., 3., 4., 5.
8. Cool and add 10 ml $H_2O_2$ dropwise.
9. Distill until fumes of $SO_3$ appear, collect the distillate.
10. Cool and add 5 ml concentrated HBr.
11. Distill until fumes of $SO_3$ appear, collect the distillate.
12. Repeat operations 10. and 11. twice.
13. Wash the cooling system and the distillation flask three or four times with 6 M HCl.

The dissolution - distillation of the irradiated samples takes normally 3.5 h.

b) Simplified Separation Scheme:

The procedure is outlined in Fig. 3 and its four steps are described below:

1. After the dissolution - distillation procedure has been performed, collect together the distillates of the fuming $HNO_3$, of the $H_2O_2$, of the HBr and the washing solutions, heat to 60-70 °C and add 35 ml of $H_2O_2$ dropwise to remove bromine. The remaining solution makes up FRACTION 1 (As, Hg, Sb, Se, Re, Ru, Ge).
2. Dry the distillation residue, cool and dissolve with 10 ml of 1 M $HClO_4$, adding 20 mg carrier of Cs, Rb, Ag and Cr. Pass through two superposed columns of AAO and Dowex 50x8 in chloridric form,

each of 10 mm in dia. and 100 mm in length.

3. Wash the columns with 40 ml of 1 M $HClO_4$ to obtain FRACTION 2 (Na, K, Rb, Cs, Ag, Cr).

4. Wash the Dowex 50 column with 30 ml of 47% HBr containing carriers of Co and Zn to elute FRACTION 3 (Co, Zn, Cu, Mn). AAO column and Dowex 50 column are respectively FRACTION 4 (P, Mo, W) and FRACTION 5 (Ca, Ba, Sr, Sc, Fe, Ga, Np).

Two hours are normally necessary to perform this separation.

The five fractions are measured either with Ge(Li) or with NaI(Tl) detectors, after 5 h decay, to determine Cu, Ga, Na, K, As, and after 2-8 days decay to measure longer-lived nuclides. FRACTION 4 is also measured with Čerenkov technique for P determination.

Table II shows in a synthetic way how the measurements are performed and gives an idea on the counting times involved.

c) Complete Separation Scheme:

The procedure is schematised in Fig. 4 and provides a selective separation of long-lived nuclides into 17 fractions.
The different steps are presented below.

1. After having performed the dissolution-distillation procedure, collect together the distillates of the fuming $HNO_3$, of the $H_2O_2$, of the HBr and the washing solutions, heat up to 60-70°C, adding drops of $H_2O_2$ up to 35 ml to drive off bromine.

2. Pass the distillate portion (about 60 ml) through two superposed columns of Dowex 1x8 in chloride form and TDO. Both columns have a diameter of 7 mm and a height of 30 mm.

3. Elute Hg (FRACTION 1) from Dowex with 25 ml of 6 M $HClO_4$.
4. Elute As (FRACTION 2) from TDO with 25 ml of 2 M HCl and 2 M $Na_2HAsO_4$.

TABLE II - Counting Times Involved in the Measurement of Fractions Obtained by the "Simplified" Separation Scheme

| FRACTIONS | FIRST MEASUREMENT NaI(Tl) 2.0h Ge(Li) 0.5h ČER. 2.0m | | | | SECOND MEASUREMENT NaI(Tl) 3.0h Ge(Li) 6.0h | | | |
|---|---|---|---|---|---|---|---|---|
| | COUNTING TECHNIQUE | ELEMENTS MEASURED | DECAY TIME | COUNTING TIME | COUNTING TECHNIQUE | ELEMENTS MEASURED | DECAY TIME | COUNTING TIME |
| 1 | NaI(Tl) | As (Hg,Re,Ru,Ge) | 5.0h | 0.5h | NaI(Tl) | Sb,Se | 2.0d | 2.0h |
| 2 | Ge(Li) | Na, K | 5.0h | 0.5h | Ge(Li) | Rb,Cs (Ag,Cr) | 8.0d | 4.0h |
| 3 | NaI(Tl) | Cu | 5.0h | 1.0h | NaI(Tl) | Co,Zn | 8.0d | 1.0h |
| 4 | ČER. | P (Pa,Mo,W) | 5.0h | 2.0m | | | | |
| 5 | NaI(Tl) | Ga | 5.0h | 0.5h | Ge(Li) | Ca,Ba,Sr,Sc Fe(Np,R.E.) | 8.0d | 2.0h |

*In parenthesis elements not detected*

5. The columns of Dowex 1 and TDO which have respectively retained Sb and Se represent FRACTION 3 and FRACTION 4.

6. Dry the distillation residue, cool and dissolve with 5 ml 6 M HCl. Pass through superposed columns of HAP (12 mm dia., 50 mm long), Dowex 1x8 (10 mm dia., 80 mm long) in chloride form and CUS (12 mm dia. and 80 mm long). In order to complete the elution of non-absorbed elements, wash the columns with 10 ml 6 M HCl, 20 ml of 4 M HCl and 10 ml of 3 M HCl.

7. The Rb (FRACTION 5) is eluted from HAP with 6 M $HClO_4$. FRACTION 6 contains Na and Ta retained on HAP.

8. From the Dowex 1 column elute:
   a) Fe, Mo, Ga, W with 20 ml of 0.5 M HCl,
   b) Zn with 20 ml of 0.02 M HCl (FRACTION 7),
   c) Cd with 20 ml of $H_2O$ (FRACTION 8),
   d) Pd with 20 ml of 6 M HCl and 1 M $ZnCl_2$ (FRACTION 9).

   The Dowex 1 column containing Au is the FRACTION 10.

9. Pass the fraction containing Fe, Mo, Ga, W through a Dowex 50x8 column (7 mm dia., 30 mm long) in chloride form. Wash with 10 ml of 0.5 M HCl: the eluate contains Mo and W (FRACTION 11). Elute Ga with 20 ml of 1 M HF with 5% ascorbic acid (FRACTION 12). Dowex 1 column containing Fe is the FRACTION 13.

10. The CUS column containing Cu is the FRACTION 14.

11. The non-absorbed fraction from the three superposed columns is dried, dissolved with 5 ml of 0.5 M $HNO_3$ and passed through a set of two superposed columns (12 mm dia., 100 mm long) of AAO and Dowex 50x8 in hydrogen form. Wash with 60 ml of 0.5 M $HNO_3$.

12. The AAO column containing P is the FRACTION 15.

13. Co, Cr, Cs and Mn (FRACTION 16) are eluted from Dowex 50 with 20 ml of concentrated HBr; Ca, Ba, Sr and Sc are absorbed on the

column (FRACTION 17).

The complete separation is performed in about five hours.

Table III gives details about the measurement of the 17 fractions obtained by this separation scheme.

TABLE III - Counting Times Involved in the Measurement of Fractions Obtained by the "Complete" Separation Scheme

| FRACTIONS | FIRST MEASUREMENT NaI(Tl) 7.0h Ge(Li) 6.0h čER. -5.0h | | | | SECOND MEASUREMENT NaI(Tl) 3.5h | | | |
|---|---|---|---|---|---|---|---|---|
| | COUNTING TECHNIQUE | ELEMENTS MEASURED | DECAY TIME | COUNTING TIME | COUNTING TECHNIQUE | ELEMENTS MEASURED | DECAY TIME | COUNTING TIME |
| 1 | NaI(Tl) | Hg | 1.0 d | 2.0 h | | | | |
| 2 | čER. | As | 1.0 d | 0.5 h | | | | |
| 3 | NaI(Tl) | Sb | 8.0 d | 1.0 h | | | | |
| 4 | NaI(Tl) | Se | 8.0 d | 1.0 h | | | | |
| 5 | čER. | K | 1.0 d | 0.5 h | NaI(Tl) | Rb | 8.0 d | 0.5 h |
| 6 | čER. | Na | 1.0 d | 3.0 m | NaI(Tl) | (Ta) | 8.0 d | 2.0 h |
| 7 | čER. | Zn | 1.0 d | 15.0 m | | | | |
| 8 | čER. | Cd | 1.0 d | 1.0 h | | | | |
| 9 | čER. | (Pd) | 1.0 d | 2.0 h | | | | |
| 10 | NaI(Tl) | (Au) | 1.0 d | 0.5 h | | | | |
| 11 | NaI(Tl) | Mo (W) | 1.0 d | 1.0 h | | | | |
| 12 | čER. | Ga | 1.0 d | 0.5 h | | | | |
| 13 | NaI(Tl) | Fe | 8.0 d | 1.0 h | | | | |
| 14 | NaI(Tl) | Cu | 1.0 d | 0.5 h | | | | |
| 15 | čER. | P | 1.0 d | 3.0 m | | | | |
| 16 | NaI(Tl) | Mn | 1.0 d | 10.0 m | Ge(Li) | Co, Cr, Cs | 8.0 d | 4.0 h |
| 17 | Ge(Li) | Ca, Ba, Sr, Sc | 8.0 d | 2.0 h | | | | |

*In parenthesis elements not detected*

## 3. RESULTS

In neutron activation analysis often the determinations of different elements are performed in a single sample. From the beginning to the end of the analysis a delay of some months may be necessary. As a consequence it appears problematic to go back to eventual accidental errors occurred during the analysis of the sample. In cases in which these errors cannot be stated, a statistical treatment of the data obtained could be helpful to suggest eventual outliers. As an indication of anomalous data the Dixon Test[12] was used.

The experimental single measurements, assuming that they belong to a normal distribution, are arranged in increasing order, as follows:

$$x_1 \leqslant x_2 \leqslant \cdots\cdots \leqslant x_n,$$

according to the number n of data available, different ratios are calculated if either $x_1$ or $x_n$ are suspected to be out of the distribution. $R_1$ refers to $x_1$ and $R_2$ refers to $x_n$.

If $n \leqslant 7$ $\qquad R_1 = \dfrac{x_2 - x_1}{x_n - x_1} \qquad R_2 = \dfrac{x_n - x_{n-1}}{x_n - x_1}$

If $7 < n \leqslant 10$ $\qquad R_1 = \dfrac{x_2 - x_1}{x_{n-1} - x_1} \qquad R_2 = \dfrac{x_n - x_{n-1}}{x_n - x_2}$

If $10 < n \leqslant 13$ $\qquad R_1 = \dfrac{x_3 - x_1}{x_{n-1} - x_1} \qquad R_2 = \dfrac{x_n - x_{n-2}}{x_n - x_2}$

If $n > 13$ $\qquad R_1 = \dfrac{x_3 - x_1}{x_{n-2} - x_1} \qquad R_2 = \dfrac{x_n - x_{n-2}}{x_n - x_3}$

Assuming a confidence level of 95% the ratios $R_1$ and $R_2$ are compared with the corresponding figures of the Dixon table for a given n : $DT_n$.

If $R_1 > DT_n$ and/or $R_2 > DT_n$

the suspected values $x_1$ or $x_n$ are rejected and new ratios are calculated with the n-i values.

The test is repeated until $R_1$ and/or $R_2$ are greater than $DT_{(n-i)}$.

The estimated mean $\bar{X}$ of the n-i values is then calculated together with its standard deviation s and its variance $s^2$.
The above mentioned operations are automatically performed by a computer program called MEAVAR, set up at the JRC Scientific Data Processing Centre.

The confidence limits are then calculated

$$\bar{X} \pm \frac{s}{\sqrt{n}} \cdot t \qquad (1)$$

where: $\frac{s}{\sqrt{n}}$ is the mean deviation

n is the number of individual measurements (after the Dixon Test is applied)

t is the Student's factor depending on the number of degrees of freedom and on the chosen confidence level (in this case 95%).

The percentage relative standard deviation:

$$\frac{100 \cdot s}{\bar{X}} \qquad (2)$$

which has been preferred over the precision, and the percentage accuracy

$$\frac{100 \cdot /\bar{X} - \hat{X}/}{\hat{X}} \qquad (3)$$

(only calculated in case of NBS certified values $\hat{X}$) are presented in the Tables IV, V and VI, which report the results obtained by this laboratory for Bovine Liver, Orchard Leaves and Tomato Leaves.

In the first column of the tables the symbols of the analysed elements are reported. In the second one certified or tentative values given by the NBS, in the third one the confidence limits obtained by (1). The fourth co-

lumn represents the percentage deviation from NBS values obtained by (3): the actual percentage accuracy is significant only when NBS certified values exist. Column five represents the percentage relative standard deviation, obtained by (2), related to the set of measurements performed in this laboratory.

The NBS Tomato Leaves not being certified, only column 1, 3 and 5 are presented in Table VI.

TABLE IV - Determination of Elements in NBS SRM 1577 (Bovine Liver)

| Element | NBS values ppm (1) | Found ppm (2) | Deviation from NBS values percentage | Percent relative standard deviation |
|---|---|---|---|---|
| As | (0.055) | 0.0585 ± 0.009(8) | (6.36) | 18.4 |
| Ca | ( 123 ) | 124.67 ± 8.48 (6) | (1.36) | 6.46 |
| Cd | 0.27 ± 0.04 | 0.246 ± 0.056(9) | 8.89 | 29.5 |
| Cl | (2600) | 2793 ± 294.4(14) | (7.45) | 18.22 |
| Co | (0.18) | 0.188 ± 0.027(11) | (4.44) | 21.32 |
| Cu | 193 ± 10 | 191 ± 10.5 (7) | 1.03 | 5.93 |
| Fe | 270 ± 20 | 260.9 ± 12.89(16) | 3.37 | 9.25 |
| Ga (*) | - | - | - | - |
| Hg | 0.016±0.002 | 0.0164 ± 0.0043(8) | 2.5 | 31.2 |
| K | 9700±600 | 9984.16 ± 647.8 (12) | 2.93 | 10.2 |
| Mg | ( 605 ) | 604.6 ± 26.84 (5) | (0.07) | 3.57 |
| Mn | 10.3± 1 | 10.17 ± 0.69 (10) | 1.26 | 9.47 |
| Mo | ( 3.2 ) | 3.78 ± 0.356 (11) | (18.1) | 14.0 |
| Na | 2430± 130 | 2609 ± 142 (14) | 7.37 | 9.44 |
| Ni | - | $\leqslant$ 0.5 | - | - |
| P | - | 13497.7 ± 290.1 (21) | - | 4.71 |
| Rb | 18.3± 1 | 18.62 ± 0.95 (11) | 1.75 | 7.58 |
| Se | 1.1± 0.1 | 1.107 ± 0.15 (4) | 0.64 | 8.55 |
| Si | - | 16.79 ± 1.84 (12) | - | 17.2 |
| Zn | 130± 10 | 137.2 ± 5.75 (24) | 5.55 | 9.93 |

(*) Due to the dishomogeneity the value is not reported (see text),

(1) In parenthesis are tentative values given by NBS,

(2) Figures in parenthesis are the number of determinations performed.

TABLE V - Determination of Elements in NBS SRM 1571 (Orchard Leaves)

| Element | NBS values ppm (1) | Found ppm (2) | Deviation from NBS values percentage | Percent relative standard deviation |
|---|---|---|---|---|
| As | 14 ± 2 | 12.15 ± 0.43 (3) | 13.2 | 1.52 |
| Cd | 0.11 ± 0.02 | 0.12 ± 0.014(10) | 9.09 | 16.3 |
| Cl | ( 700 ) | 690 ± 0.0 (4) | ( 1.43 ) | 0. |
| Co | ( 0.2 ) | 0.112 ± 0.017(11) | ( 44.0 ) | 22.55 |
| Cr | ( 2.3 ) | 1.97 ± 0.44 (9) | ( 14.34 ) | 29.2 |
| Cs | - | 0.0374 ± 0.011 (6) | - | 28.0 |
| Cu | 12 ± 1 | 12.62 ± 0.85 (4) | 5.16 | 4.24 |
| Fe | 300 ± 20 | 311.1 ± 10.4 (20) | 3.7 | 7.15 |
| Ga | - | 0.078 ± 0.025 (9) | - | 42.4 |
| Hg | 0.155 ± 0.015 | 0.146 ± 0.017 (7) | 5.81 | 12.6 |
| K | 14700 ± 300 | 14375 ± 794 (4) | 2.21 | 2.45 |
| Mg | 6200 ± 200 | 6173.8 ± 179 (4) | 0.44 | 1.29 |
| Mn | 91 ± 4 | 91.6 ± 1.08 (6) | 0.66 | 1.12 |
| Mo | - | 0.327 ± 0.07 (9) | - | 27.9 |
| Na | 82 ± 6 | 81.8 ± 1.83 (5) | 0.24 | 1.8 |
| Ni | 1.3 ± 0.2 | 1.28 ± 0.16 (7) | 1.54 | 13.45 |
| P | 2100 ± 100 | 2096.7 ± 70.14 (6) | 0.20 | 3.19 |
| Rb | 12 ± 1 | 11.28 ± 0.42 (20) | 5.91 | 7.95 |
| Se | 0.08 ± 0.01 | 0.0798 ± 0.008 (5) | 0.25 | 8.05 |
| Si | - | 475.8 ± 12.29 (6) | - | 2.46 |
| Sr | ( 37 ) | 44.2 ± 2.85 (11) | (19.46 ) | 9.55 |
| Zn | 25 ± 3 | 25.07 ± 0.76 (17) | 0.28 | 5.75 |

(1) In parenthesis are tentative values given by NBS,

(2) Figures in parenthesis are the number of determinations performed.

TABLE VI - Determination of Elements in NBS Tomato Leaves

| Element | Found ppm (1) | Percent relative standard deviation |
|---|---|---|
| Ba | 56.5 ± 11.24 (6) | 18.1 |
| Ca | 27058 ± 2064 (7) | 8.22 |
| Cl | 10850 ± 1201 (4) | 6.95 |
| Co | 0.4 ± 0.106 (10) | 37.0 |
| Cr | 3.107 ± 1.08 (9) | 45.1 |
| Cu | 14.1 ± 5.64 (3) | 16.05 |
| Fe | 469.25 ± 118.3 (8) | 30.5 |
| Ga | 0.0693 ± 0.067 (3) | 39.0 |
| Hg | 0.128 ± 0.118 (3) | 37.0 |
| K | 44272.7 ± 2816 (11) | 9.45 |
| La | 0.346 ± 0.079 (6) | 21.7 |
| Mn | 209.18 ± 9.93 (8) | 5.66 |
| Na | 459.0 ± 46.1 (11) | 15.5 |
| P | 3420 ± 89.5 (3) | 1.05 |
| Rb | 15.16 ± 1.35 (9) | 11.6 |
| Sc | 0.208 ± 0.089 (11) | 63.6 |
| Sr | 65.5 ± 5.84 (8) | 10.7 |
| Zn | 58.03 ± 3.33 (7) | 6.2 |

(1) Figures in parenthesis are the number of determinations performed.

- Bovine Liver

The accuracy is good for the elements certified by the NBS while the deviation from the suggested values is fairly good. Only for Mo the deviation is larger than 10%. The relative standard deviation for ten elements is better than 10%; for As, Cd, Cl, Co, Hg, Mo, Se and Si it exceeds 10%. This could be due either to the small number of determinations performed, or to the low content of these elements in the sample.

The analysis of Ga has given rise to two series of results corresponding to the two different specimens:

I - 72 0.13 ; 0.13 ; 0.15 ; 0.16 ; 0.18; 0.22 ; 0.23 ; 0.31 ppm

I - 649 0.0066 ; $\leqslant$ 0.01 ; 0.05 ; 0.009 ppm.

An estimated mean value has not been reported for this element.

- Orchard Leaves

The accuracy is better than 10% for all the certified elements, except As (13.2%). The value for this last element is in fact still doubtful[13, 14, 15]. The deviation from the NBS uncertified elements is generally large, except for chlorine.

The relative standard deviation is better than 10% for 13 elements; for Cd, Co, Cr, Cs, Ga, Hg, Mo and Ni it exceeds 10%. The concentrations of these elements in the sample are very low and in some cases such as for Cd, Mo and Ni is near to the sensitivity limits of our technique.

- Tomato Leaves

During the course of certification analyses, the homogeneity of the material was questioned[44] and the Tomato Leaves were withdrawn. The

high relative standard deviation obtained by our analyses may be therefore due to inhomogeneity, although the small number of analyses performed does not allow definite conclusions.

## 4. DISCUSSION

### 4.1 Dissolution and Distillation

Reagents currently used for wet ashing of organic materials are $H_2SO_4$, $HNO_3$, $HClO_4$ and $H_2O_2$, mainly utilised in two components mixtures such as $H_2SO_4$ - $H_2O_2$, $H_2SO_4$ - $HNO_3$, $HClO_4$ - $HNO_3$, $HNO_3$ - $H_2O_2$.

A more detailed description of the different dissolution methods and of the destruction mechanisms of the organic materials can be found in the literature[16].

In order to avoid eventual explosions $HClO_4$ has been left out of our wet ashing procedure mixtures.

When the use of $H_2SO_4$ was necessary for successive distillations in our separation schemes, the mixture $H_2SO_4$ - $HNO_3$ was used to dissolve organic samples. In the selective determination of Ca, Mg, Ni and Si we have used the mixture fuming $HNO_3$ - $H_2O_2$.

The advantage of obtaining a rapid organic mineralisation by $H_2SO_4$ and $HNO_3$ is partly diminished by the difficulty of removing $H_2SO_4$. Besides, for materials rich in Ca, the eventual precipitation of $CaSO_4$ could incorporate other elements.

In our working conditions we have never noted the formation of such precipitates. During the dissolution phase a quantitative distillation is only obtained for Cl, Br and I. Ge, Ru and Os distillate only partially, while As and Se partly distillate in the presence of large quantities of chlorides which are normally absent in biological materials. In order to avoid possible losses of material through volatilisation during dissolution, the distillate obtained during this operation, is collected together with the products of successive distillations with $H_2O_2$ and HBr.

The relatively low boiling point of the mixture (120°C) makes it ne-

cessary to extend its boiling period in order to obtain complete mineralisation.

Distillation of volatile elements in $H_2SO_4$ - HBr solution is a procedure currently used by several authors[17, 18, 19]. We have, however, repeated the distillation recovery tests with radioactive tracers because modifications of the apparatus and of the procedures were unavoidable.

In Table VII radiochemical yields for volatile elements obtained in this laboratory are given, together with those of some elements which could become volatile in particular conditions.

TABLE VII

| Element | Percent chemical yield | Element | Percent chemical yield |
|---|---|---|---|
| As | > 99 | Re | > 98 |
| Au | < 0.5 (*) | Ru | 91 |
| Cr | < 0.5 | Sb | 98 |
| Hg | > 95 | Se | > 99 |
| Os | > 99 | Sn | > 92 |

(*) 10 mg carrier

To perform a quantitative distillation (>95%) of Ru it was necessary to use $KIO_3$ in the last distillation step.

Generally, the presence of $^{82}Br$ does not allow the direct counting of the distillate. Br is drawn away by heating up to 60°C with $H_2O_2$. Also Cl, I and Os volatilise in these conditions.

4.2 Determination of Ca, Mg, Ni and Si

Analysis of Ca, Mg, Ni and Si by neutron activation and Čerenkov counting technique has been recently set up in this laboratory[20]. Neutron activation analysis with gamma ray spectrometry is not sufficiently sensi-

tive in this case.

The Čerenkov counting efficiencies are 59% for $^{49}Ca \rightarrow ^{49}Sc$, 53.3% for $^{27}Mg$, 20.5% for $^{65}Ni$ and 40.5% for $^{31}Si$ (see Table I). As a consequence, the counting sensitivity of the Čerenkov technique compared to the area of the most prominent gamma peaks of the same radioisotope obtained by 3"x3" NaI(Tl) detectors is increased about 13 times for Mg, 35 times for Ni, 13,800 times for Si. $^{49}Sc$ being a pure beta-emitter, the increase of sensitivity compared to $^{47}Ca$ can be assumed to be about 1,000 times considering the activities at saturation.

In the examined biological samples the activities of $^{49}Sc$, $^{27}Mg$, $^{65}Ni$ and $^{31}Si$ are masked by those of $^{24}Na$, $^{56}Mn$, $^{42}K$, $^{38}Cl$, $^{82}Br$, $^{32}P$ and others. The interfering activities are removed by selective separations with good decontamination factors, as described above.

4.3 Simplified Separation Scheme

The number of elements which can be determined in the studied samples by non-destructive analysis and gamma ray spectrometry is rather limited. Due to possible interferences, the identification of some elements is also doubtful.

Radionuclides such as $^{24}Na$, among the short-living ones, and $^{32}P$ among longer-lived radioisotopes restrict the use of gamma ray spectrometry; besides, $^{46}Sc$ interferes with $^{65}Zn$, $^{65}Zn$ interferes with $^{85}Sr$, $^{124}Sb$ with $^{134}Cs$, etc.

To avoid these drawbacks we have set up a simplified separation procedure.

In this laboratory problems involving the presence of great quantities of $^{32}P$ in biological material were successfully solved by using columns of AAO[21].

In this scheme the elution of $^{24}Na$ and $^{42}K$ allows the determination of $^{72}Ga$ and $^{64}Cu$. We also have carefully avoided that mixtures of Sc and Zn, Zn and Sr and Sb and Cs were in the same fraction.
The residue, dissolved in 1 M $HClO_4$ is passed through AAO where P, Mo and W are retained, then through Dowex 50 where Ca, Ba, Sr, Sc, Fe, Ga, Np, Co, Zn, Cu are absorbed while Na, K, Rb, Cs, Ag and Cr are eluted[22].

If Cu must be determined, a further separation is obtained by eluting Co, Zn and Cu from Dowex 50 with concentrated HBr[38]. The composition of the mixture of radionuclides on the resin is such, that it can be counted by a Ge(Li) detector.

We have noticed that the behaviour of Cr and Fe sometimes differs from the expected one. Cr in some cases is partially absorbed on the Dowex 50 column, while about 5% of Fe is eluted from the same column. With the simplified separation scheme it has been possible to determine five short-lived isotopes (Na, K, Cu, Ga and As) and thirteen long-lived isotopes (P, Ca, Ba, Sr, Sc, Fe, Rb, Cs, Cr, Co, Zn, Sb and Se).

4.4 Complete Separation Scheme

The scope of this separation procedure is twofold:

a) increase the number of elements to be determined;
b) increase the sensitivity by the use of less selective but highly sensitive counting techniques.

The use of the Čerenkov countings, in particular, requires more selective separation procedures. To avoid errors due to incomplete separations, the control of the decay of the radioisotopes to be determined is recommended. As a consequence, only short-lived radionuclides were determined by us with this counting technique.

Several separation procedures for biological matrices and for other

radiochemical applications, are reported in the literature[18, 23-38].
Our separation scheme takes advantage of the ionic exchange of anionic and cationic resins and of the absorption properties of some ionic precipitates studied in this laboratory[39].

The distillation residues in 6 M HCl are passed through HAP, Dowex 1 and CUS columns. On the HAP column Na, Rb, K and Ta are retained[40]; the apparent disagreement between what was stated by Girardi and Sabbioni[35] (75% of Rb retained) and this work (100% of Rb retained) is due to the greater quantity of HAP used in the present procedures.

The elution of Rb and K with 6 M $HClO_4$ and carriers, allows the counting of the two elements with the Čerenkov technique with a considerable increase of sensitivity. Also Na, retained on HAP can be counted in the same way.
The passage through Dowex 1 and the elution in hydrochloric media based on the studies of Kraus and Nelson[41] is a step commonly used by us and by several other laboratories.
Fractions containing Zn, Cd and Pd are all counted with the Čerenkov technique.

The 0.5 M HCl fraction containing Fe, Ga and Mo must be further split into three different fractions as the presence of Fe (coloured solution) either gives rise to the quenching phenomenon during Čerenkov counting for Ga determination, or does not allow the analysis of $^{99}Mo$, this radioisotope having its higher peak (140 keV) at the energy of a gamma peak of $^{59}Fe$.

Cu is selectively retained on CUS[39].

The eluate of the three columns mainly contains $^{32}P$ which is in turn retained together with Pa on AAO.

Ca, Ba, Sr, Sc, Co, Cr, and Cs are absorbed on Dowex 50[42] and then by elution with 48% HBr, split into two groups[43].

It seemed to us not convenient to further split the eluates into other groups as the gamma spectra are sufficiently equilibrated to be counted with Ge(Li) detectors. Besides, the separation could become extremely long and complicated.

The distillate is passed through Dowex 1 which retains Sb and Hg and through TDO where Se and As are absorbed[39]. The elution of Hg is sometimes necessary due to the presence of large amounts of Sb; As must be removed from TDO if Čerenkov countings must be performed.

The complete separation scheme allowed the determination of Na, K, Zn, Ga, Cu, As among the short-lived elements (up to 24 h) and of Rb, Cs, Cd, Fe, Mo, Ca, Ba, Sr, Sc, Co, Cr, Sb, Hg, Se and P among the long-lived elements.

The lack of adequate standards of Au, Pd, and W has not allowed their determination even if their presence in some samples has been noticed.

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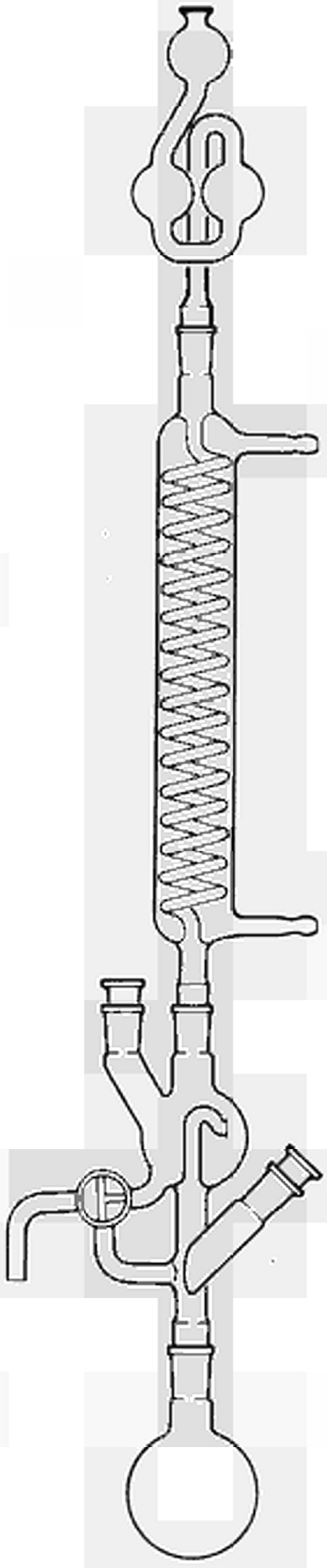


Fig. 1 - Dissolution and Distillation Apparatus - Dimensions are given in mm.

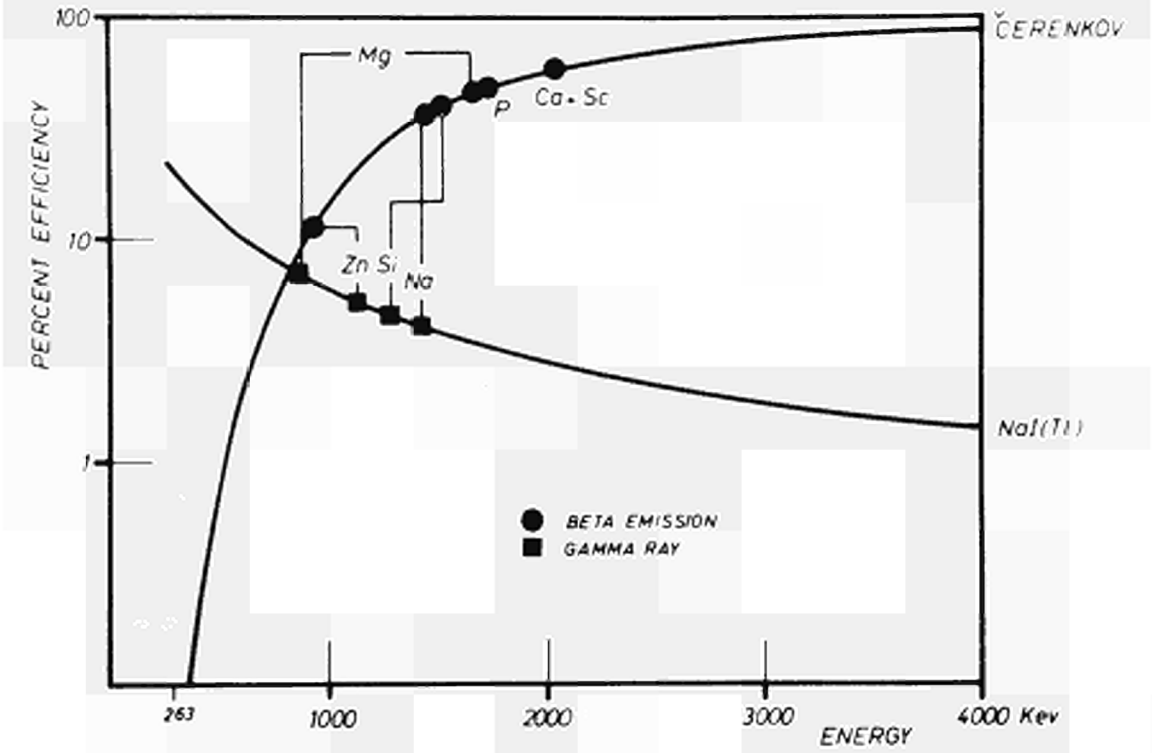


Fig. 2 - Comparison between Čerenkov and NaI(Tl) Counting Efficiencies vs. Energy

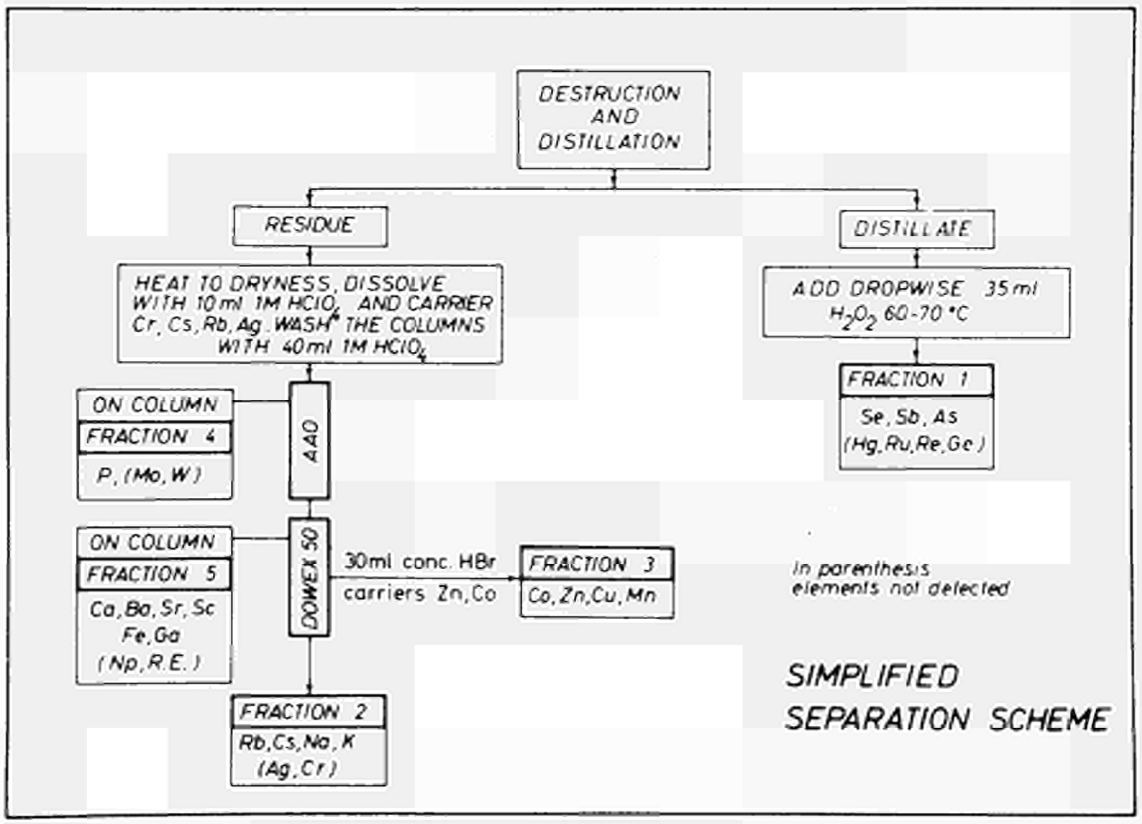


Fig. 3 - "Simplified" Separation Scheme

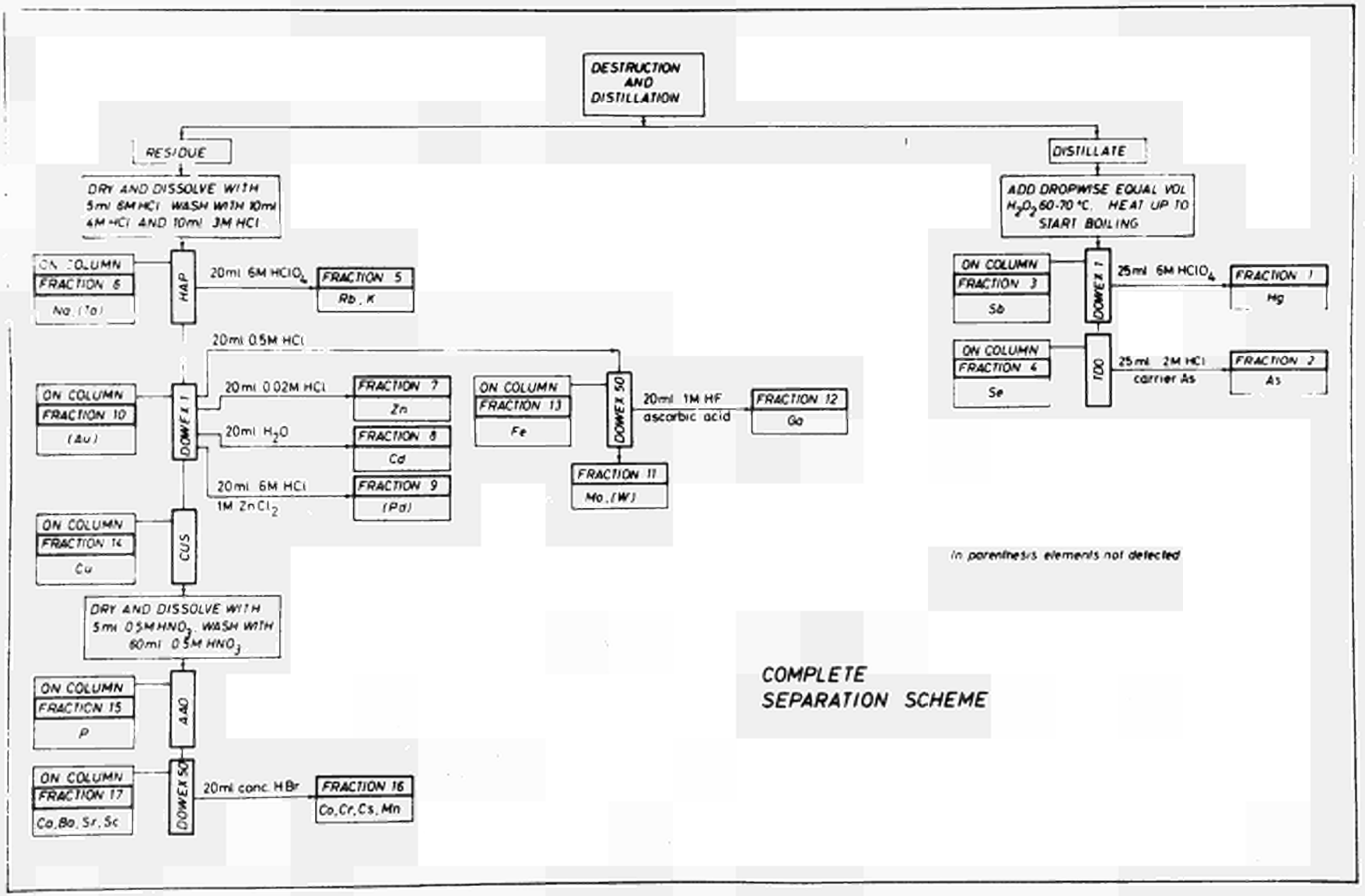


Fig. 4 - "Complete" Separation Scheme

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